5. DISCUSSION

This section discusses the results from the reporting period in the context of the overall effectiveness of the ISB remedy. Section 5.1 presents a summary of the major field results, while Section 5.2 discussed the overall effectiveness of the ISB remedy. Section 5.3 describes the impact of ISB on the secondary source, and Section 5.4 discusses the persistence of t-DCE. The results of the AED lab studies are discussed in Section 5.5.

5.1 Summary of Field Test Results

This section provides a summary of the major field results. As described in the previous ISB Annual Performance Report (INEEL 2002a), monitoring data indicated that the sodium lactate injection strategy used during PDP-II did not achieve the desired distribution of electron donor within the source area. While efficient ARD was occurring in the area surrounding the injection well, this area of biological activity did not encompass the entire secondary source in the downgradient direction, as evidenced from the continued flux of TCE to downgradient wells TAN-37A, TAN-37B, TAN-28, and TAN-30A. Therefore, several alternative sodium lactate injection strategies were employed during the current reporting period in an attempt to achieve the desired electron donor distribution using a single injection well. The initial strategy used double the volume (2X) of the standard PDP-II injection and a 3% sodium lactate solution. After two injections (October 30, 2001, and January 2, 2002), the next injection (March 2002) again doubled the volume (4X) and also doubled the concentration (6% sodium lactate). A small volume (1X) 6% injection was performed on July 1, 2002 as an interim measure. Finally, the last two injections of the reporting period (July 30, 2002, and October 1, 2002) used the same volume as the March 2002 injection but half the concentration (3%).

In general, the sodium lactate injections used during the reporting period successfully delivered lactate to the immediate source area. Also, the 4X 6% injection delivered significant concentrations of lactate to deep wells TAN-26 and TAN-37C for the first time since the field evaluation. In addition, electron donor was observed at TAN-D2. However, donor was not observed at downgradient wells TAN-37A, TAN-37B, TAN-28, or TAN-30A during the reporting period.

Redox conditions within the source area and deep wells remained methanogenic throughout the reporting period. In downgradient wells, sulfate generally persisted throughout the reporting period. The presence of sulfate at these wells indicates that the biologically active zone does not encompass the entire residual source area in the downgradient direction. While these wells also showed significant levels of methane, this methane is a result of transport from active methanogenic areas upgradient. Since the 4X 6% injection delivered electron donor to TAN-D2 (an upgradient well), the consistent absence of sulfate and increase in methane levels indicate methanogenic conditions at this location.

Anaerobic reductive dechlorination continued in source area wells as a significant process. In TSF-05A and TSF-05B, spikes in TCE were observed during sampling rounds immediately following each injection as a result of enhanced mass transfer from the residual source to the aqueous phase. In most cases, TCE concentrations were below detection limits by the following sampling event (~4 weeks later). Despite these fluctuations in TCE levels, ethene remained the dominant compound at these wells. At TAN-25 and TAN-31, while TCE has remained below detection, cis-DCE has represented a larger fraction of the total VOCs since the March 2002 4X 6% injection. Ethene at both locations was lower than observed prior to the March 4X 6% injection and has continued to drop since that time.

5.2 Effectiveness of the In Situ Bioremediation System

As stated in Section 2, the objectives of PDO were to optimize ISB remedy operations, including evaluating electron donor utilization pathways and altering injections of electron donor to eliminate flux of VOCs in the downgradient direction. During PDP-I, propionate was the primary electron donor at TAN, which resulted in the most efficient ARD ever observed, as indicated by the molar ratio of TCE to ethene and the chlorine number. In general, a decline in ARD efficiency was observed within the TAN source area after PDP-I. This decline was characterized by a rebound in TCE concentrations and chlorine number in well TAN-37, in addition to a rebound in cis-DCE concentrations and chlorine number in wells TAN-25 and TAN-31. In order to mitigate this trend, a detailed evaluation of electron donor utilization, distribution, and factors affecting ARD efficiency was performed.

5.2.1 Lactate Degradation Pathways

The ARD efficiency loss after PDP-I correlated to a decline in the propionate to acetate ratios in TAN-25 and TAN-31. During the field evaluation, sodium lactate injections initially resulted in the production of propionate and acetate in a stoichiometric ratio of 2:1, indicating that lactate fermentation occurred primarily through the propionate pathway (see Section 4.1.1). Lactate was rapidly utilized, and propionate and acetate accumulated before they were slowly degraded. During PDP-I, accumulated propionate was the primary electron donor as sodium lactate injections were discontinued, which resulted in the most efficient ARD of TCE ever observed. Recent sodium lactate injection data, however, suggest that while propionate production is still prevalent, acetate production from lactate fermentation is becoming more significant, as indicated by the declining propionate to acetate ratios. Published models suggest the lactate to acetate pathway supports less efficient ARD than does the lactate to propionate pathway because it favors hydrogen-utilizing methanogenic activity, which competes with hydrogen-utilizing dechlorination (see Figure 4-1). Also, a molecular microbial community characterization of TAN-25 groundwater indicated that homoacetogenic bacteria, likely responsible for the fermentation of lactate to acetate, predominate the bacterial community. As predicted by the published models, a general decrease in ARD efficiency, qualified as increases in cis-DCE concentrations and the chlorine number, was correlated with the increased utilization of lactate via the acetate pathway. Figures 5-1 and 5-2 show this correlation as an overall decline in the propionate to acetate ratio, an increase in cis-DCE, and a decline in ethene concentrations that occurred in PDP-II and PDO compared with PDP-I in TAN-25 and TAN-31. Two possible remedies for this trend were explored: one was to test different injection strategies in an attempt to favor the propionate pathway, and the other was to evaluate several AEDs (including propionate) in laboratory experiments to determine if they support more efficient ARD (Section 5.5). The impact of the alternate injection strategies is discussed below.

5.2.2 Lactate Utilization

One tool used to evaluate electron donor utilization was the first order degradation rate constant. Calculations were performed for data obtained during regular ISB operations (Section 4.1.1.2) and for data collected during the tracer test (Section 4.4.4). The difference between the two sets of rate estimates was that the tracer test estimates were derived from relatively continuous COD and VFA curves, while the ISB operations rate estimates were essentially derived from two data points; one approximately 1 week after an injection and the other approximately 5 weeks after an injection. Since the tracer test was performed in conjunction with a 4X 3% injection, the tracer test rate estimates from TAN-25 and TAN-31 can be compared to the ISB operations rate estimates derived from the 4X 3% injection and possibly from other injections as well.

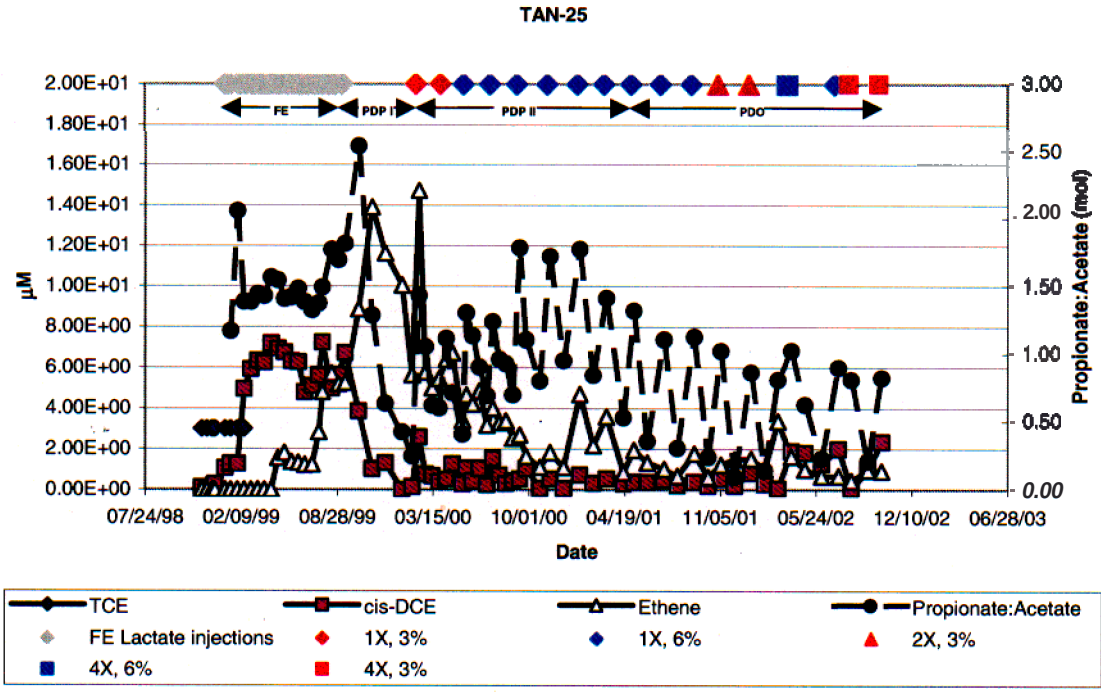

Figure 5-1. Correlation between propionate:acetate, cis-DCE, and ethene in TAN-25.

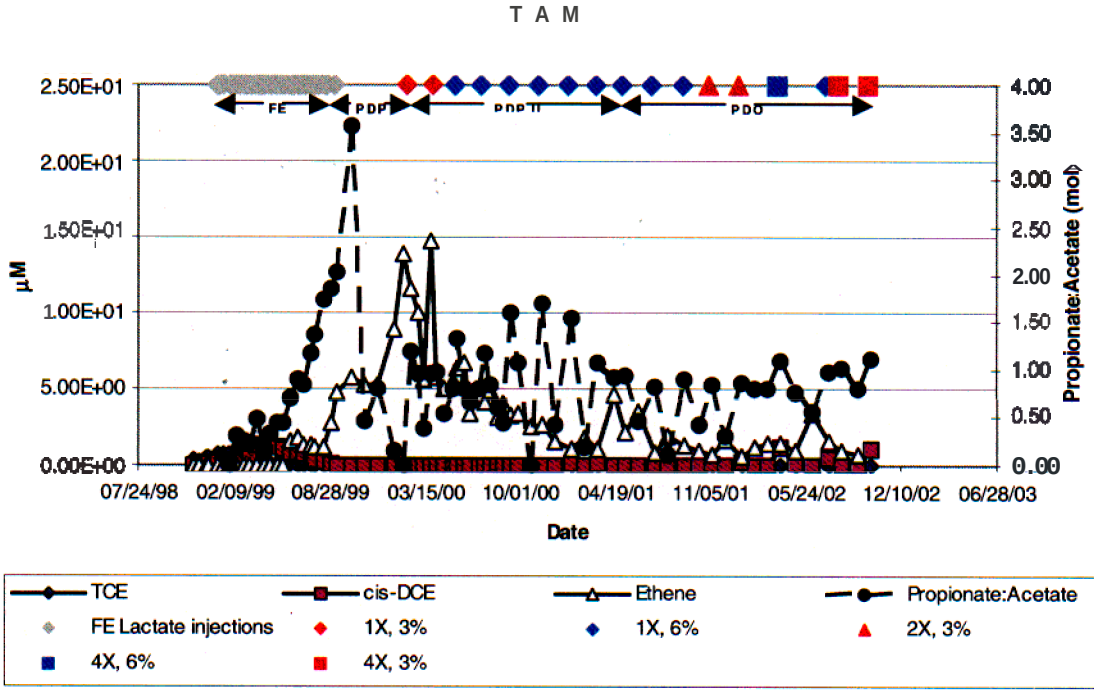

Figure 5-2. Correlation between propionate:acetate and TCE, cis-DCE, and ethene in TAN-31.

Table 5-1 shows the lactate degradation rate constants derived from the tracer test and from ISB operations data for TAN-25 and TAN-31. From Table 5-1, the electron donor degradation rate constants were generally similar for the ISB operations and tracer study data for TAN-25. Conversely, in TAN-31, the rate constants were higher for the tracer study than the ISB operations data. The reasons the TAN-31 rate constants were dissimilar are likely related to the amount of lactate that actually reached TAN-31 and the point in time at which data were collected. During regular ISB operations, the first data point is typically measured a week after lactate injection, and the next data point is usually collected nearly a month later. Likely, sodium lactate has long since been depleted at the second data point, which skews the rate calculation conservatively. As an example, after the July 2002 lactate injection, lactate went from 1,245.1 mg/L in TAN-31 to 0.117 mg/L one month later. In the tracer test data collected during this same injection, the lactate concentration in TAN-31 one day after injection was 16,223.75 mg/L, which was depleted to 96.8 mg/L nine days after injection. Therefore, lactate is probably depleted nearly 2 weeks before the second data point is collected during regular ISB operations, which would explain why the rate constant calculated during the tracer study was nearly twice that of the highest rate constant collected with the ISB data.

Table 5-1. First order lactate degradation rate constants from in situ bioremediation operations and the tracer test.

Well	Sept. 2001 1X 6%	Oct.30, 2001 2 x 3%	Jan.2, 2002 2 x 3%	Mar.25, 2002 4X 6%	Jul.30, 2002 4 x 3%	Oct.1,2002 4 x 3%	Tracer Test
TAN-25	0.33	0.28	0.33	0.18	0.29	0.18	0.33
TAN-31	0.08	0.15	0.20	0.15	0.26	0.31	0.51

The lactate degradation constant was generally higher for TAN-31 than TAN-25 for both data sets. This suggests that lactate was degraded faster at TAN-31 than TAN-25. First order kinetics assumes that the degradation of electron donor is only a function of concentration, which implies the degradation rate constants should be the same for all data. In order for this to be true, however, all conditions (i.e., temperature and redox) must be constant both spatially and temporally during all injections. Several factors, however, introduced variability in wells TAN-25 and TAN-31, most of which were associated with the electron donor injections themselves. For example, several lactate injection strategies have been used during this reporting period, each of which has involved varying volumes of lactate and potable water. The larger volume injections introduced more aerobic water and had more of an impact on the rates near the injection point. Thus, the injection of aerobic water into the treatment area likely affects TAN-25 more than TAN-31, resulting in slower degradation until sufficiently anaerobic conditions are re-attained.

5.2.3 Alternate Injection Strategies

Different injection strategies were performed and monitored (Section 4.1) with the goal of achieving the high ARD efficiency observed during PDP-I. The goal of the injections was to increase the lactate distribution to the edge of the residual source area, to stimulate efficient ARD within this area, and to cut off flux of chlorinated solvents outside the residual source area. The injection strategies applied to the TAN hot spot included 1X (~12,000 gal), 2X (~24,000 gal), and 4X (~48,000 gal) volume injections at 3 and 6% sodium lactate concentrations (as presented in Section 4.1). Overall, these different injections had distinctive effects on the distribution of electron donor, the electron donor utilization (although the propionate to acetate ratio was not impacted), the redox conditions, and ARD efficiency within the treatment area.

Each of the four injection strategies distributed lactate differently within the treatment cell. The 1X 6% injections performed September 5, 2001, and July 1, 2002, resulted in very similar concentrations

of lactate in source area wells TSF-05A, TSF-05B, TAN-25, and TAN-31, but did not result in the detection of lactate in any other wells. The 2X 3% injections performed October 30, 2001, and January 2, 2002, resulted in increased lactate concentrations within the source wells, with a particularly high increase observed at TSF-05A. The higher concentration observed at TSF-05A was likely due to the decreased lactate utilization resulting from injecting twice the volume of aerobic water into the anaerobic treatment zone.

The March 25, 2002, 4X 6% injection resulted in the highest lactate concentrations observed within the source wells and deep well TAN-26, the first-ever detection of significant propionate and acetate in upgradient well TAN-D2, and the highest propionate and acetate concentrations observed in downgradient well TAN-37C since the field evaluation. Electron donor, however, was not detected in significant concentrations in downgradient wells TAN-37A, TAN-37B, TAN-28, and TAN-30A. Therefore, the area impacted by electron donor following this injection did not appear to encompass the entire secondary source. The utilization rate of lactate for the source area wells was also the lowest following this injection than for any other injection. Again, the higher volume aerobic injection likely impacted the anaerobic treatment zone requiring an increased lag period before rapid lactate fermentation began. The utilization rates of propionate and acetate in the source wells also decreased after this injection, which was likely the result of inhibition due to residual lactate within the system. This injection did not, however, impact the downgradient and outside wells, as TCE concentrations in these wells remained relatively constant.

The July 30, 2002, and October 1, 2002, sodium lactate injections resulted in the highest lactate concentrations observed in wells TAN-25 and TAN-31 over the course of ISB operations, with the exception of the March 2002 injection. Conversely, the lactate concentrations within the TSF-05 injection well were lower during these 3% injections than for the 6% injections. The lactate utilization rates for source wells TSF-05 and TAN-25 were also lower for the 4X injections than were observed for the 1X and 2X injections, but were much higher for TAN-31. The increased utilization rates observed in TAN-31 were likely due to the relatively high concentrations of lactate that were distributed to this well as compared with the 1X and 2X injections. The 4X injections appear to have resulted in somewhat of a trade-off in that the distribution of lactate throughout the residual source area was increased due to the increased volume of the injections, but the higher volumes of injected aerobic water temporarily decreased ARD efficiency near TSF-05.

All injection strategies used during the reporting period did not result in stimulating sufficient biological activity to successfully cut off the flux of TCE from the residual source, as TCE concentrations within downgradient wells TAN-37A and TAN-37B, TAN-28, and TAN-30A remained relatively constant throughout the reporting period. The ARD efficiency near the injection point also appeared to decline with the 4X injections, as cis-DCE was detected in higher concentrations at TAN-25 and TAN-31 than had been observed for nearly 1.5 years (Figures 5-1 and 5-2). This was likely due to impacts of aerobic injection water traveling farther within the treatment zone and negatively impacting ARD.

Although the area impacted by the lactate injections increased as a result of the higher volumes and lower lactate utilization rates, it appears that the overall objective of distributing electron donor throughout the entire residual source area was not met during this reporting period, as evidenced by the continued chloroethene flux to downgradient wells. In addition, the ARD efficiency near the injection point has apparently declined, although sufficient treatment capacity still exists to completely dechlorinate the TCE that is mobilized to TAN-25 and TAN-31 from the residual source. The 4X injection also did not have a significant impact on the lactate degradation pathway, as measured by the propionate to acetate ratio. Thus, an alternate injection strategy, possibly including installation of additional injection well at the presumed downgradient edge of the residual source or the use of another electron donor, remains necessary to achieve TAN ISB performance objectives.

5.3 Impact of In Situ Bioremediation on Source

5.3.1 Effective Porosity

The results of the tracer test and water level monitoring during lactate injections were used to draw conclusions about the impact of ISB operations on the secondary source material surrounding TSF-05. As described in Section 4.4, the tracer test was performed in order to provide data necessary to support the development of a predictive modeling tool that could be used to test various electron donor injection strategies. The execution of the tracer test provided the opportunity to estimate the effective porosity both within and on the edge of the source area. These data were then compared to those from the 1998 Tracer Test to identify changes in porosity as a result of 4 years of ISB operations.

In addition to the tracer test, a qualitative analysis of the peak mounding observed in wells TAN-25 and TAN-31, in response to sodium lactate injections, was performed to indicate whether there had been any changes over time. While the volume of each injection will obviously affect the observed mounding, a comparison of the relative mounding seen in TAN-25 and TAN-31 for the same injections can identify effective porosity changes along the respective flow paths. As shown in Figure 4-36, the difference in peak mounding seen in TAN-25 and TAN-31 has decreased over time so that both TAN-25 and TAN-31 show similar peak mounding for each injection. This change in relative peak mounding response suggests that there may have been porosity changes in the source area over time.

As described in Section 4.4, the tracer test data, while not entirely conclusive, do appear to suggest that the effective porosity along the flow path from TSF-05 to TAN-25 may have increased relative to 1998 values, while the effective porosity values along the flow path from TSF-05 to TAN-31 were relatively similar to 1998 values. In addition, the water level data collected during injections qualitatively suggest that effective porosity may have increased between TSF-05 and TAN-31. These results suggest that the ISB operations over the past 4 years have had an impact on the secondary source material in the source area. The implications of this observation are that the ISB activities are actively reducing source material, which ultimately accelerates the overall cleanup effort at TAN.

5.3.2 Metals and Radionuclide Monitoring

The PDO Work Plan (INEEL 2002b) identified monitoring the concentrations of metals and radionuclides in order to ensure that ISB operations did not result in the enhanced mobilization of these species above acceptable levels. To meet this PDO objective, concentrations of gamma emitters, alpha emitters, metals, and strontium were monitored at seven wells during the reporting period. Source area monitoring included TSF-05A, TSF-05B, TAN-25, and TAN-31; conditions deep in the aquifer were monitored at TAN-26; downgradient monitoring was conducted at TAN-28; and outside monitoring at TAN-29. Tritium was monitored at all ISB wells.

The results of this monitoring during the reporting period are presented in Section 4.1.6. As described in Section 4.1.6, Cs-137 and Sr-90 were detected above MCLs in source area and downgradient wells. While TSF-05B had elevated alpha emitter levels, concentrations at TAN-28 and TAN-29 were below MCLs. Strontium levels in source area wells fluctuated at levels consistent with data from the previous reporting period, while concentrations in TAN-28 and TAN-29 remained low and reasonably constant. Tritium concentrations were below MCLs throughout the treatment cell. The results of metals analyses were compared to MCL values where MCLs were established. The results indicate that chromium was above MCL values in wells TSF-05B and TAN-25 in a single sampling event; however, concentrations in TAN-28 and TAN-29 were below the MCL of 100 µg/L.

The results of the radionuclide and metals monitoring during the reporting period indicate that ISB activities have not resulted in enhanced migration of these compounds above acceptable levels. While there are some examples of elevated concentrations in a localized area surrounding the TSF-05 injection well, all concentrations consistently decrease with distance from TSF-05. The data illustrated in Figure 4-37 were used to derive a trend line relating Sr-90 activity and distance from TSF-05, as shown in Figure 5-3. Figure 5-3 illustrates that the average Sr-90 concentrations decreased from approximately 1,203 pCi/L at TSF-05 to 34 pCi/L at TAN-29, which is 152 m (500 ft) downgradient. This decrease is attributed to sorption, dispersion, precipitation, and radioactive decay. The attenuation of Sr-90 over distance is important since the MCL of 8 pCi/L must not be exceeded at TAN-40 where contaminated groundwater is pumped for treatment at the NPTF (see Section 4.1.6). Assuming the Sr-90 continues to follow the same attenuation trend between TAN-29 and TAN-40 (TAN-40 is 109 m [358 ft] downgradient of TAN-29), Figure 5-4 shows that a Sr-90 concentration greater than 103 pCi/L at TAN-29 would be required to result in the MCL of 8 pCi/L being exceeded at TAN-40. Since the average Sr-90 concentration of 34 pCi/L at TAN-29 results in an estimated Sr-90 of 2.6 pCi/L at TAN-40, Sr-90 mobilization is not a significant problem for ISB operations at this time.

5.4 Persistence of trans-DCE

As described in Section 4.1.3, trans-DCE has persisted in the treatment cell since the onset of ISB operations. In general, concentrations of trans-DCE have remained steady in source area wells and appear to decrease downgradient. As of October 2002, the highest concentration within the treatment cell (around 435 µg/L) was at TSF-05A. Some fluctuation in concentrations was observed at TAN-37A and TAN-37B, but as of October 2002 concentrations were near the MCL value of 100 µg/L. While TAN-28 showed a concentration of 170 µg/L in October 2002, trans-DCE was below the MCL at TAN-29, the downgradient edge of the ISB treatment cell.

It is thought that the trans-DCE in the treatment cell is a result of its presence as an original contaminant in the secondary source and possibly as a result of its generation during the biological degradation of TCE. Even though trans-DCE appears relatively recalcitrant to degradation compared to cis-DCE, other attenuation processes result in the reduction of concentrations to acceptable levels at the downgradient edge of the ISB treatment cell, as indicated by the results from TAN-29. Given this, continued monitoring of trans-DCE throughout the treatment cell is recommended at this time. Also, it is recommended that a laboratory microcosm study be performed to evaluate the biodegradation rate of trans-DCE relative to that of cis-DCE.

5.5 Cost-Effectiveness of the In Situ Bioremediation Monitoring Program

One of the objectives identified in the PDO Work Plan was to optimize ISB sampling frequency and analytes. Sampling was conducted monthly throughout the reporting period, with a core analyte set collected each month. Additional analyte sets were collected less frequently during the reporting period (refer to Table 3-4 for definitions of ISB analyte sets). This section presents a qualitative analysis of the sampling frequency, as well as the utility of each analyte set collected during the reporting period.

The monthly analyte set consisted of IRC sample VOCs (TCE, PCE, c-DCE, t-DCE, and VC), ethene/ethane/methane, and propionate/butyrate/acetate/lactate; field test kits, ferrous iron, sulfate, alkalinity, and COD; tritium, which was analyzed at an off-Site laboratory; and gamma screens analyzed at the RML. All of these analytes are essential to assessing the performance of the ISB remedy, and the monthly frequency is still justified throughout interim and initial operations when the remedy is still being optimized. Therefore, all monthly analytes remain necessary at this time.

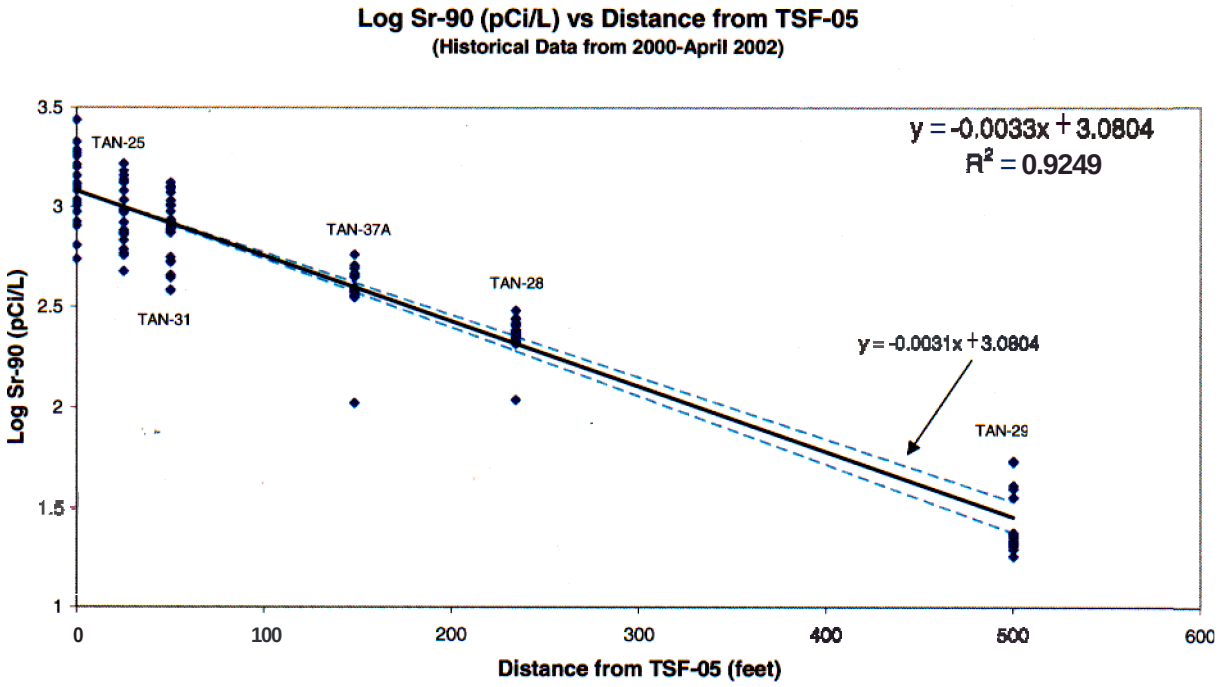

Figure 5-3. Sr-90 activity versus distance trend line.

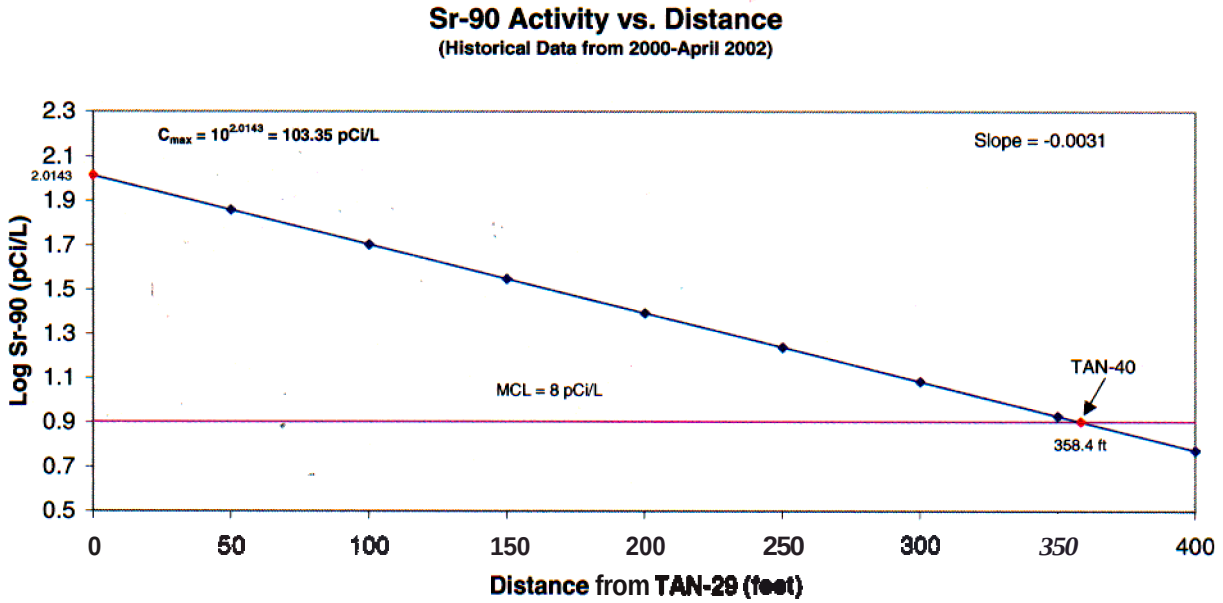

Figure 5-4. Estimated Sr-90 activity versus distance between TAN-29 and TAN-40.

The nutrient analyte set consisted of the field test kits phosphate and ammonia, which were analyzed semiannually during the reporting period. These analytes provide useful data regarding the presence/absence of macronutrients during ISB operations and should continue to be collected on a semiannual basis. The field standard additions analyte set was added during the middle of the reporting period to improve QA/QC in the field laboratory. These analytes provide useful data regarding the precision and accuracy of the field test kits and therefore should continue to be collected for every sampling round that employs field test kits.

The splits analyte set consisted of quarterly VOCs (TCE, PCE, c-DCE, t-DCE, and VC) and ethene/ethane/methane samples sent to off-Site laboratories and analyzed using EPA-approved methods. The purpose of these samples is to confirm the IRC laboratory results obtained using the solid-phase microextraction (SPME) method. The splits analyte set is moderately useful if the off-Site laboratory and the IRC report similar results, but it is less useful if the results are significantly different. The reason for this is that splits provide no way to determine which laboratory is reporting the more accurate results. In addition, the splits analyte set represents a fairly significant cost for the off-Site analytical services, and the sample collection has proven somewhat difficult due to sample preservation requirements. In contrast, a PE sampling program does provide the desired information because it entails sending certified standards to a laboratory for purposes of assessing accuracy.

According to the ISB Remedial Action Work Plan (DOE-ID 2003a), the quality level of the VOC data collected during performance monitoring of the first three phases of the ISB remedy will be screening with definitive confirmation. According to the *Quality Assurance Project Plan for Waste Area Groups 1, 2, 3, 4, 5, 6, 7, 10, and Inactive Sites* (DOE-ID 2002b), this data quality level requires that at least 10% of the screening data (i.e., IRC) be confirmed using definitive data (i.e., off-Site laboratory). Since monthly sampling is still ongoing, VOC splits can be reduced to a semiannual frequency and still meet the definition of the data quality level specified in the Remedial Action Work Plan. However, no definitive confirmation for ethene/ethane/methane samples is required by the Remedial Action Work Plan during any ISB phase. Therefore, it is recommended that the frequency of VOC splits be reduced to semiannual, ethene/ethane/methane splits be eliminated altogether, and that a PE sampling program be initiated for VOCs analyzed at the IRC laboratory.

The analyte sets metals, Sr-90, and gamma spectroscopy were collected quarterly from a subset of seven monitoring locations to monitor the potential mobilization of metals and radionuclides from the hot spot. From Section 4.1.6, metals were detected only at TSF-05B, TAN-25, and TAN-31; of these, only chromium was detected above its MCL. Thus, it is recommended that metals samples no longer be collected because sufficient historical data now exist to demonstrate that ISB operations have not resulted in mobilization of metals from the hot spot.

Sr-90 concentrations have increased due to ISB operations but only in the vicinity of TSF-05 (refer to Section 4.1.6.3). With the exception of TAN-37, the downgradient and outside wells have remained near pre-ISB levels. Gamma spectroscopy sampling has resulted in Cs-137 detections in TSF-05A, TSF-05B, TAN-25, and TAN-31, but no gamma-emitters were detected in the downgradient and outside wells. Since TAN-29 is the furthest downgradient ISB well, it can serve as a sentinel monitoring point for mobilization of radionuclides from the hot spot. Therefore, it is recommended that Sr-90 and gamma spectroscopy be collected quarterly from TAN-29 only, rather than from the subset of seven wells monitored during the current reporting period.

Gross alpha samples were collected once during the reporting period in November 2002. The data from that sampling round, as well as the previous annual gross alpha sampling round (November 2001), showed that gross alpha activity was not detected above the MCL of 15 pCi/L in any TAN well. In addition, gross alpha has been identified as an analyte in the MNA monitoring program. Gross alpha

samples will be collected annually at wells TAN-25, TAN-28, TAN-29, TAN-30A, TAN-37A, TAN-37B, TSF-05A, and TSF-05B during the performance operations phase of the MNA remedy (DOE-ID 2003b). Thus, the need to collect gross alpha samples as a part of ISB sampling no longer exists, and it is recommended that they be discontinued.

The bromide and iodide analytes sets were only collected during the 2002 Tracer Test and are not collected as a part of ISB sampling. The microbiological analyte sets were collected on an as-needed basis to support ongoing laboratory studies, including those being conducted to evaluate AEDs. These samples should be collected as needed during hture operations.

Although it is not explicitly denoted as an analyte set, the final category of data collected during ISB operations is multi-parameter water quality instrument data, both from in situ deployments and from purge monitoring. The in situ multi-parameter water quality instrument data provide valuable information regarding the arrival of electron donor, as measured by increases in specific conductance. They also provide usehl data on the general geochemistry of the groundwater in the ISB treatment cell. The use of multiparameter water quality instruments for purge monitoring essentially provides real-time samples of pH, ORP, dissolved oxygen, temperature, and specific conductance, all of which are usehl parameters.

Hydrolab instruments were used to collect nearly all multiparameter water quality instrument data during this reporting period. However, the Hydrolab network has proven to be expensive and difficult to maintain and operate. Because of this, it has been gradually replaced with a network of In Situ Troll 9000 instruments, which provide the same geochemistry data as the Hydrolabs, but potentially offer several operational advantages. Therefore, it is recommended that the Troll network be used to replace the Hydrolab network, and that one or more Hydrolab instruments be kept onsite for use as a backup to the Trolls.

5.6 Alternate Electron Donor Laboratory Studies

As described in Section 3.6, the objective of the laboratory studies was to determine if AEDs were more efficient and/or cost-effective than sodium lactate for use during long-term ISB operations at TAN. This section discusses the results of the laboratory studies presented in Section 4.5.

5.6.1 Anaerobic Reductive Dechlorination Efficiency

One component of this assessment was to compare ARD efficiency of TAN-derived laboratory cultures between AEDs feed-grade molasses, food-grade molasses, cheese whey, and sodium lactate. Section 4.5.1 presents the results that are discussed below.

The first step in the study process was to develop a TCE-dechlorinating enrichment culture using sodium lactate. Once this culture was developed, aliquots were used to determine the effect of AEDs on the dechlorination ability of the enrichment. The development of the initial bioreactor cultures revealed the difficulty of getting multiple bioreactors to behave in a similar fashion, even under similar conditions. After many months of operation under identical conditions, dechlorination rates were different in all bioreactors. This created some uncertainty when drawing conclusions about the AED flask study since the same phenomenon could account for the differences observed between the different AEDs. The flask portion of the study, however, had the advantage of starting with a common consortium that was adapted to laboratory conditions, and, therefore, differences in the dechlorination measured in the flasks were most likely related to the differences in the carbon sources.

The results of the AED study provided usehl information regarding applicability of AEDs to the TAN field site. Initial analyses of the AED flasks after 1 year of operation indicated complete

dechlorination to ethene in all flasks. The dechlorination ability of the different cultures was then more closely monitored over a 5-month period to assess the potential differences in dechlorination rate and electron donor utilization. This analysis indicated different rates of dechlorination depending on the carbon source. Sodium lactate stimulated the most rapid, complete dechlorination of TCE to ethene. This was not surprising, given that the field site from which the groundwater was obtained was from TAN ISB wells, and that sodium lactate was used as the electron donor in the development of the initial bioreactor enrichments. After sodium lactate, food-grade molasses showed the next best dechlorination rate followed by cheese whey. The feed-grade molasses was the only carbon source that did not facilitate dechlorination of all amended parent compounds (TCE and PCE) during the 5-month study; thus, it had the lowest dechlorination rate.

In terms of cost-effectiveness measured as cost per unit of TCE converted to ethene, food-grade molasses was the most cost-effective electron donor, followed by feed-grade molasses, sodium lactate, and then cheese whey. The costs of sodium lactate and food-grade molasses, however, were overestimated because electron donor (as propionate) was still present in the culture at the end of the study. It is important to note that this method of evaluating cost-effectiveness accounts only for the rate of dechlorination in terms of ethene production but does not account for incomplete dechlorination of parent compounds, as discussed in Section 4.5.1. Thus, in terms of the field application at TAN, it remains uncertain whether the reduced cost of food-grade molasses would be offset by longer remedial time frames due to the lower rates of ARD.

5.6.2 Interfacial Tension Analysis

Interfacial tension analyses were performed using various AED solutions to assess their ability to enhance TCE solubility compared to that of high concentration (30 to 60%) sodium lactate. It has been demonstrated that some electron donors, including sodium lactate, decrease IFT when injected at high enough concentrations, thereby accelerating TCE dissolution from the residual source (Sorenson 2002). The process is referred to as Bioavailability Enhancement Technology (B.E.T.™) (patent pending). Therefore, IFT was measured for various alternated electron donors and compared with sodium lactate. Out of 10 AEDs evaluated, seven had significant IFT reductions and easily formed solutions or emulsions that could be potentially delivered to the subsurface. These included ethyl lactate, molasses, whey powder, unpurified dairy product, sodium dipropionate, and LactOil™. These results indicate that a variety of AEDs may be better at enhancing the solubility of TCE than sodium lactate, and consequently reduce the remedial timeframe of the TAN hot spot.

5.6.3 Molecular Analysis

As described in Section 3.6.3, the main objective of this study was to determine potential impacts of AEDs feed-grade molasses, food-grade molasses, and cheese whey on the sodium lactate enriched, TCE-dechlorinating community. The ability of each AED culture to dechlorinate TCE was significantly different (Section 4.6.1). Therefore, it was hypothesized that these differences in dechlorination ability may have been due to differences in the community structure, specifically the lack of dechlorinating bacteria within the culture.

According to T-RFLP analysis, all of the communities analyzed were significantly different. More species were found in the lactate culture than in any of the AED cultures, as described in Appendix E. In addition, the food-grade molasses culture was more similar to the lactate culture than either the feed-grade molasses or cheese whey cultures. The impurity of the cheese whey and feed-grade molasses may have introduced bacterial populations not originally present within the TAN groundwater. These foreign populations may have contributed to the low TCE-dechlorination performance observed within these cultures. Consequently, the introduction of foreign populations into the groundwater at TAN may have

significant implications to the natural dechlorinating populations. Therefore, the use of electron donors with active cultures should be carefully considered. If the AED does not work in the field, it may be difficult to recover the lactate-derived community because the introduced bacterial populations may out-compete the previous populations.

The differences observed within the communities may also have been due to differences in potential electron donors derived from the parent donors. Feed-grade molasses, food-grade molasses, and cheese whey are all complex electron donors comprised of a variety of chemicals that could potentially be fermented in microbial metabolic reactions. Lactate, conversely, is a simple electron donor whose fermentation pathways have been identified (see Figure 4-1). The fermentation of lactate produces acetate, propionate, and hydrogen as secondary electron donors. Thus, the introduction of the AEDs and their fermentation by-products were likely selected for different populations within the communities, which were better adapted to using the different substrates.

All of these electron donors, however, inevitably produce hydrogen during various anaerobic fermentation reactions. *Dehalococcoides ethenogenes* is an obligate hydrogenotroph and dechlorinator, which may be why this organism was present in all of the AED cultures as one of the dominant species. The prevalence of hydrogen and TCE would have provided strong selective pressure for this organism. Thus, this bacterium may be supported by a variety of different cultures using different electron donors as long as the fermentations produce hydrogen and the redox conditions allow for dechlorination of the chlorinated ethenes. The predominance of this species within all of the cultures suggests that the ability to completely dechlorinate TCE was not limited by a reduction or absence of dechlorinating bacteria within the AED cultures. Other factors that could have influenced the TCE dechlorination performance within the AED cultures include competition between other microbes and dechlorinating bacteria for limited nutrients, the production of substances that are inhibitory to dechlorination, and/or a mutation of the dechlorinating bacteria so they can no longer dechlorinate one or more of the chlorinated ethenes. These potential effects cannot be identified without hrther study.

5.6.4 Metals Analysis

As described in Section 3.5.4, the purpose of this portion of the studies was to determine if any of the potential AEDs had above 10 x MCLs at the injection concentration. Sodium dipropionate was the only AED that violated the metals concentration threshold, as it had lead above 10 x MCL (refer to Appendix E for all AED metals results). However, given its performance in other portions of the AED evaluation, and given that additional processing steps could be performed to address its lead content, it was recommended that sodium dipropionate be included for hrther evaluation.

5.6.5 Alternate Electron Donor Evaluation Protocol

The AED laboratory studies supported the development of a standardized approach for evaluation of potential AEDs for use in bioremediation efforts. This approach consists of five major components described below. This process has been formalized in a work plan to guide hture AED evaluations (INEEL 2003c).

- First, a relatively simple initial screening of the AED relative to sodium lactate is performed based on published facts. This screening includes a cost-benefit analysis to compare the unit cost for the AED relative to the unit cost of sodium lactate, an evaluation of the physical properties of the AED that may indicate whether or not it will perform better in the field than sodium lactate, and an evaluation of field logistical issues.

- Second, lab studies will be performed for each AED based on the data gaps that are apparent after the initial screening. These lab studies may include, among others, enhancement of TCE solubility (IFT), TAL metals content, phase of AED (aqueous vs. nonaqueous), suspended solids content, the propensity to form emulsions and/or oily substances that may not disperse in an aquifer environment, the ability of the AED to stimulate ARD of TCE to ethene, and the impact of the AED on the microbial community.

- Following the completion of all the laboratory studies, the third step in the evaluation process is to determine if all necessary criteria defined for the laboratory studies have been met, and if so, whether a limited scale field pilot test should be considered.

- Once an AED has been selected, the fourth step is to implement a field pilot test using the AED These field studies will be typically limited to a relatively small geographic area (i.e., within approximately 50 to 75 ft of the field study injection well).

- The fifth step is to evaluate the performance of the AED in the field pilot test and decide if the AED should replace sodium lactate as the electron donor for bioremediation at TAN.

6. CONCLUSIONS

In general, the ISB system continues to operate effectively, stimulating ARD throughout most of the source area. Ethene was present in significant concentrations in all the source area wells, indicating active ARD. Also, the large volume (4X) injections resulted in an increase in the biological area of influence within the source area, as indicated by increased concentrations of electron donor in wells TAN-25 and TAN-31. Downgradient, the response in redox conditions in TAN-37A and TAN-28 indicated that the large volume injections had some impact on the downgradient portion of the source; however, the continued flux of sulfate and TCE to these wells indicates that the size of the biologically active zone does not fully encompass the entire residual source in the downgradient direction.

In an attempt to create the appropriate distribution, the injection of large masses of electron donor has resulted in extremely reducing conditions in the source area wells, which favor a very successful homoacetogenic population. This has resulted in an overall increase in the utilization of the lactate → acetate and H_2 pathway at the expense of the lactate → propionate and acetate pathway. This shift can be correlated to a decrease in ARD efficiency in the source area. Despite this, complete ARD to ethene is still occurring in the source area wells.

Also, the injection of increased volumes of aerobic potable water appeared to result in a temporary decline in ARD efficiency following each sodium lactate injection. Following each of the high volume (4X) injections, a significant increase in cis-DCE concentrations in source area wells TAN-25 and TAN-31 was observed. These spikes in cis-DCE indicate a short-term decline in ARD efficiency resulting from the negative impact of the aerobic water on the anaerobic microbial community following each injection. Cis-DCE concentrations returned to pre-injection levels following each spike as efficient ARD resumed.

The 4 years of sodium lactate injection and resulting biological activity in the TSF-05 area have resulted in the destruction of source material, as indicated by changes in the effective porosity, based on the results of the tracer test and modeling activities and the observed groundwater mounding surrounding well TSF-05. The implication of this conclusion is that the ISB remedy is actively reducing the source of contamination at the TSF-05 hot spot.

The ability to enhance the dissolution of the residual source at TAN through the B.E.T.™ mechanism was an essential factor contributing to the acceptance of ISB as the hot spot remedy. The results presented herein indicate that many AEDs displayed reduced IFT at high concentrations, and that hrther evaluation of sodium dipropionate, LactOil™, ethyl lactate, and whey powder is recommended. Also, these studies supported the development of a standardized approach for evaluation of potential AEDs for use in bioremediation efforts. This approach consists of five major components, as described in Section 5. This process has been formalized in a work plan to guide hture evaluations (INEEL 2003c).

7. RECOMMENDATIONS

7.1 Overall Recommendations

The overall recommendation made in this report is to continue to optimize the electron donor distribution in order to achieve complete and efficient ARD throughout the entire secondary source. There are several actions that can be considered during this optimization activity, as follows:

- Continued manipulation of the sodium lactate injection volume and concentration to achieve the desired electron donor distribution using a single injection well (TSF-05).
- Evaluation of technologies with the potential to improve the distribution and mixing of electron donor within the source area.
- Installation of an additional injection well at the presumed downgradient edge of the secondary source. Predictive modeling has been used to locate the new injection well. The use of this well in combination with TSF-05 would likely be quite effective in achieving the desired electron donor distribution.
- The newly refined ISB model should be used to determine optimum electron donor injection strategies using TSF-05 and the additional injection well.
- Use the results of the tracer test to improve the predictive capabilities of the model for additional optimization activities.
- Reduce the frequency of VOC splits to semiannual, eliminate ethene/ethane/methane splits, and implement a PE sampling program for VOC samples analyzed at the IRC laboratory.
- Eliminate all radiological samples except for monthly tritium samples collected from all ISB wells and quarterly Sr-90 and gamma spectroscopy samples collected from TAN-29 only.
- Replace the Hydrolab network with a Troll 9000 network and continue to collect multiparameter water quality instrument data and purge monitoring data.
- Evaluate the rate of ARD of trans-DCE relative to cis-DCE in laboratory microcosm studies.
- Finally, consider the use of an AED that will avoid potential competition effects with nondechlorinating organisms while still accelerating source degradation. Additional laboratory studies of potential donors may be required before hrther evaluation in a field pilot test.

7.2 Alternate Electron Donor Laboratory Studies Recommendations

Recommendations from the ARD efficiency study include:

- The developed laboratory culture capable of complete ARD of TCE to ethene should be used in any hture optimization studies supporting TAN OU 1-07B. This would minimize hture problems with inconsistency of cultures due to variation in culture development.

- Feed-grade molasses should no longer be considered as a replacement for sodium lactate in the field application at TAN due to its relatively low rate of dechlorination and the persistence of parent compounds observed during the study.

- Food-grade molasses should be considered for further analyses and/or field-testing to assess its potential to replace sodium lactate. Although it stimulated somewhat lower dechlorination rates, it might prove to be more cost-effective than sodium lactate.

- Liquid whey should not be considered for further evaluation because the cost comparison suggested that it was more expensive than sodium lactate. However, alternative forms of whey that may be more cost-effective should be tested in the laboratory.

- Recommendations from the IFT study include:

- Ethyl lactate could potentially be used as an additive to sodium lactate or other AED in order to increase the IFT reduction beyond what sodium lactate alone can achieve.

- Molasses, whey powder, and unpurified dairy carbohydrate should be further evaluated because they displayed larger IFT reductions than did sodium lactate.

- LactOil™ should also be considered further, both because of its extremely low IFT as well as its potential for being a slow-release electron donor.

- Sodium dipropionate should be considered further despite its lead content in excess of the allowable limit because of its extremely low IFT as well as its potential for being a slow-release electron donor. The manufacturing process for sodium dipropionate should be investigated to determine whether or not the lead content could be reduced.

In summary, the AED lab studies conducted thus far support the continued evaluation of the following AEDs, either as single products or possibly as combinations of products:

- Food grade molasses

- Wheypowder

- Unpurified dairy

- Ethyl lactate

- Sodium dipropionate

- LactOil™.

8. GUIDANCE FOR FUTURE REPORTING

As described in Section 1 and Figure 1-2, the series of phases for operation of ISB following PDO include Interim Operations, Initial Operations, Optimization Operations, and Long-Term Operations. The general performance and compliance monitoring objectives for operation of the ISB remedy component were established in the Remedial Acton Work Plan (DOE-ID 2003a), which took effect in November 2002. These include:

Compliance Objectives

- Reduce downgradient flux from the hot spot such that VOC concentrations are less than MCLs in TAN-28 and TAN-30A
- Reduce crossgradient flux from the hot spot such that VOC concentrations are less than MCLs in TAN-60 (PMW-1) and TAN-61 (PMW-2)
- Maintain the reduction of downgradient and crossgradient flux of VOCs from the hot spot below MCLs.

Performance Objectives

- Achieve electron donor distribution and associated biogeochemical reactions throughout the hot spot
- Achieve source degradation

Further, the Remedial Action Work Plan (DOE-ID 2003a) also established criteria for the completion of each of the phases of operation. These criteria, along with the activities for each phase required in order to meet the performance and compliance monitoring objectives, are presented in Table 8-1. Future reports will be prepared with the objective of evaluating progress of ISB against these performance and compliance monitoring objectives and the criteria established in the Remedial Action Work Plan and summarized in Table 8-1.

It is suggested that hture reports follow the general format used in this report, consisting of introduction, objectives, activities performed, results, discussion, conclusions, and recommendations. Also, all the data collected since the beginning of ISB operations should be included electronically on a CD, and the data for the reporting period—with the exception of in situ monitoring data—should be attached to the report in an appendix.

able 8-1. In situ biorem liation performance and compliance monitoring objectives.

Remedy Phase	Monitoring Phase/Deci: n Types[a,b]		Criteria for completion of the Phase	
Objective	Performance	Compliance		Notes
erim Operations Continue system operations to reduce contaminant flux from the hot spot	Routinely monitor performance of the ISB system with respect to indicator parameters including VOCs, tritium, ethene/ethane/methane, redox parameters, electron donor, bioactivity, and nutrients; determine whether or not operational changes are required.	N/A	Completion is defined as startup of the final remedy treatment system	
itial Operations This phase will focus on reducing the flux of VOCs from the hot spot in the downgradient direction. During this phase, data will also be gathered and analyzed relating to achievement of long-term performance objectives.	Routinely monitor performance of the ISB system with respect to indicator parameters including VOCs, tritium, ethene/ethane/methane, redox parameters, electron donor, bioactivity, and nutrients; determine whether or not operational changes are required.	Monitor concentrations of VOCs at TAN-28 and -30A for a period of one year to verify concentrations remain below MCLs.	Determine that for a period of 1 year, downgradient flux from the hot spot has been reduced such that VOC concentrations remain less than MCLs, as measured at TAN-28 and -30A.	Initial ops starts with completion of construction.
otimization Operations This phase will focus on reducing the flux of VOCs from the hot spot in the crossgradient direction, while maintaining VOC flux reduction in the downgradient direction. During this phase, data will continue to be gathered and analyzed relating to achievement of long-term performance objectives.	Routinely monitor performance of the ISB system with respect to indicator parameters including VOCs, tritium, ethene/ethane/methane, redox parameters, electron donor, bioactivity, and nutrients; determine whether or not operational changes are required.	Monitor concentrations of VOCs at PMW-1 and PMW-2 for a period of one year to verify concentrations remain below MCLs.	Determine that for a period of 1 year, crossgradient flux from the hot spot has been reduced such that VOC concentrations remain less than MCLs as measured at PMW-1 and PMW-2.	Optimization starts at the end of initial ops. The completion of optimization operations will lead to a Remedial Action Report and a functional and operational determination. Performance and compliance monitoring reports periodic with frequency no less than every 5 years.
ng-term Operations This phase will focus on achievement of hot spot source degradation, while maintaining the reduction of VOC flux from the hot spot in the crossgradient and downgradient directions.	Routinely monitor performance of the ISB system with respect to indicator parameters including VOCs, tritium, ethene/ethane/methane, redox parameters, electron donor, bioactivity, and nutrients; determine whether or not operational changes are required.	N/A	The completion criteria for long-term operations will be specified in the ISB Remedial Action Report	Performance and compliance monitoring reports periodic with frequency no less than every 5 years. Long-term operations start at the completion of optimization.

Decision Types are inputs to the DQO Process described in the *Groundwater Monitoring Plan for the Test Area North Operable Unit 1-07B ISB Remedial Action* (INEEL 2003b).
VOCs: PCE, TCE, cis- and trans-DCE, vinyl chloride
dox parameters: pH, ORP, dissolved oxygen, ferrous iron, sulfate, and methane
ectron donor: COD, specific conductivity, lactate, acetate, propionate, butyrate
oactivity: alkalinity
utrients: ammonia, nitrogen, orthophosphate.

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Appendix A

In Situ Bioremediation Field Work Details

Appendix A

In Situ Bioremediation Field Work Details

This appendix includes information that **supports** topics discussed in Section **3,** "Activities Performed." These topics included sampling deviations from planned Sampling and Analysis Plan (SAP) tables, issues pertaining to operational support activities, dates and times of TSF-05 pump placements and sampling, curtailment of daily inspections, and waste management **issues.**

I. Sampling Deviations

Deviations **from** the planned sample collections, identified in **in** situ bioremediation (ISB) **SAP** tables (Appendix B) for the reporting period, are **listed** chronologically in Table **A-1. The** planned dates **for** collecting samples were listed as **the** first day of the sampling week on the SAP tables. In most cases, sampling was not completed in 1 day; therefore, the actual sampling dates are listed in Section 3, Table **3-3.** If the planned date listed on the **SAP** table was not the **first day** of the sampling **week,** then the correct date is listed as a deviation, as shown **in** Table **A-1** . Deviations from planned analyses are presented in **Table A-2.**

Table **A-1.** Deviations from in **situ** bioremediation **Sampling** and Analysis Plan tables for **the** reporting period.

Date	Sample Number	Deviation	SAP Table Name
August 6-8, 2001	1PO15301MB 1PO15302MB 1PO15303MB 1PO15304MB 1PO15305MB 1PO15501MB 1PO15701MB 1PO15801MB 1PO15901MB 1PO16001MB 1PO16101MB 1PO16201MB	**Samples** added for microbiological analysis from **TAN-25, TAN-31,** TAN-37A, TAN-37B, **TAN-28,** TAN-30A, **TAN-29,** and **TAN-10.4.**	TAN_PDO-8/01, **Rev. 2.0**
August 7, 2001	1PO15306MB	Additional microbiological sample not needed from TAN-25.	TAN–PDO-8/01, Rev. 2.0
September 10, 2001		First day of sampling was September 10, 2001. SAP table lists planned **date** as September 3, 2001.	TAN_PDO-9/01, Rev. 1.0
September 10, 2001	1PO18101VA	Field blank sample added for volatile organic analysis (VOA).	TAN_PDO-9/01, Rev. 1.0
September 10-11, 2001	1PO17001MB 1PO17002MB 1PO17003MB 1PO17004MB 1PO17201MB 1PO17401MB 1PO17501MB 1PO17601MB 1PO17701MB 1PO17801MB 1PO17901MB	**Samples** added for microbiological **analysis from TAN-25,** TAN-31, TAN-37A, TAN-37B, TAN-28, TAN-30A, **TAN-29,** and TAN-10A.	TAN_PDO-9/01, Rev. 1.0

Table A-I. (Continued).

Date	Sample Number	Deviation	SAP Table Name
September 11, 2001	1PO17005MB 1PO17006MB	Additional microbiological samples were not needed from TAN-25.	TAN_PDO-9/01, Rev. 1.0
October 10,2001	TPD01503EG TPDO1503VA	Additional trip blank samples were not needed for Ethane/Ethene/Methane and VOA because only two deliveries were made to the INEEL Research Center (IRC), rather than the projected three deliveries.	TAN_PDO-10/01, Rev. 1.0
December 4,2001	TPD20303MB TPD20304MB	Additional microbiological samples were not needed from TAN-25.	TAN PDO-12/01. Rev. 0.0
January 7,2002	TPD31201MB	One additional microbiological sample was collected from TAN-37B.	TAN_PDO-1/02, Rev. 0.0
January 7, 2002	TPD31603VA TPD31603EG	Trip blank samples were mistakenly left out of the IRC delivery for VOA and ethane/ethane/methane.	TAN_PDO-1/02, Rev. 0.0
February 4,2002	TPD41601VA	Trip blank sample was not used, instead trip blank sample TAS00301VE was shipped with VOA samples.	TAN_PDO-2/02, Rev. 2.0
March 4,2002	TPD502011N TPD502013A TPD50201A1 TPD50201C5 TPD50201EG TPD50201R5 TPD50201R8 TPD50201VA	TSF-05B was not sampled due to an inoperable pump.	TAN_PDO-3/02, Rev. 2.0
March 4,2002	TPD51503EG TPD51503VA	Trip blank samples were mistakenly left out of the IRC delivery for VOA and ethane/ethane/methane.	TAN_PDO-3/02, Rev. 2.0
April 3,2002	TPD60303MB	Additional microbiological sample was not needed from TAN-25.	TAN_PDO-4/02-1, Rev. 4.0
April 30,2002	PD500303MB	Additional microbiological sample was not needed from TAN-25.	TAN_PDO-4/02-2, Rev. 4.0
May 1,2002		Sulfate analysis was inadvertently omitted for TSF-05B.	TAN_PDO-4/02-2. Rev. 4.0
May 8,2002	T250009MB T250010MB T250011MB	Additional microbiological samples not needed from TAN-25.	TAN-25_INTERIM
June 4,2002	PD600302MB PD600303MB	Additional microbiological samples were not needed from TAN-25.	TAN_PDO-6/02-1, Rev. 3.0
June 4,2002	PD601602EG PD601603EG	A trip blank sample was mistakenly left out of one of the deliveries and the additional trip blank was not needed,	TAN–PDO-6/02-1, Rev. 3.0
June 24,2002		Sampling event was cancelled. Thirteen sampling events were scheduled for the entire Calendar Year 2002 and only 12 were needed.	TAN_PDO-6/02, Rev 1.0
July 8,2002		First day of sampling was July 8,2002. SAP table lists planned date as July 22, 2002. Date changed because previous sampling event was cancelled.	TAN_PDO-7/02, Rev. 3.0

Table A-1. (Contir ed).

Date	Sample Number	Deviation	SAP Table Name
July 8, 2002	PD7001011N PD7008011N	Lactate samples were collected from TAN-31 and **TSF-OSA,** but broken before analysis.	TAN_PDO-7/02, Rev. 3.0
July 8,2002	PD700801VA	Only one sample voa vial was collected for the TAN-30A **VOA** to be delivered to the TRC, rather than the projected two voa vials.	TAN_PDO-7/02, Rev. 3.0
August 6,2002	PD801603EG PD801603VA	**Additional trip** blank samples were not needed for Ethane/Ethene/Methane and **VOA** because sampling took place over 2 days rather than **the** projected 3 days.	TAN_PDO-8/02, Rev. 4.0
August 6,2002	PD801701VA	There **was** confusion about whether or not to use PE samples due to possible improper refrigeration. It was decided not to use **the** PE samples **and** they were returned to the **company** that prepared them. It ended up that the samples were properly refrigerated, but the error lied in miscommunication between package receiving at Central Facilities Area and the ISB Sampling **Team.**	TAN_PDO-8/02, Rev. 4.0
September 9,2002	**PD901702EG** PD901702VA **PD901703EG** PD901703VA	Sampling was completed in one day; so additional trip blanks **were** not needed.	TAN_PDO-9/02, Rev. 3.0
September 9,2002	PD901001D1 PD901101D1	Collection **of** iodine samples from **TAN-37A** and €3 added **per** technical lead **request.**	TAN_PDO-9/02, Rev. 3.0
October 8, 2002	PD1009D1 PD1010D1	Collection **of** iodine samples from TAN-37A and B added **per** technical lead request.	TAN_PDO-10/02, Rev. 0.0

Date	Issue
December 12,2001	Alkalinity samples exceeded holding time for **TAN-IOA,** -27, -29, and -37B.
May 7,2002	No sulfate analysis result **was** recorded for TSF-05B.
May 20,2002	Lactate **was not** analyzed for interim samples collected from **TAN-37A,** -B, and -C on April 17,2002.
July 8,2002	Lactate samples **were** collected from TAN-31 and TSF-05A but were broken before analysis.

II. In Situ Bioremediation Operational Support Activities Issues

Issues directly affecting ISB sampling are detailed in Table A-3.

Table A-3. Issues directly affecting in situ bioremediation sampling.

Date	Issue
August 9-13 September 2001	Well maintenance activities took place at TAN-27, TAN-28, TAN-29, TAN-30A, TAN-31, and TAN-37. Maintenance tasks included pulling and examining the riser pipe/submersible pump to look for evidence of corrosion and installing stainless-steel riser pipe and water level access pipe at TAN-27, TAN-28, TAN-30A, and TAN-37. TAN-29 did not have an installed system to remove, so a pump and riser pipe were installed. At TAN-31, galvanized riser pipe was replaced with stainless steel riser pipe. Video logging was performed at TAN-27 and TAN-37. Additional information is available in the Bechtel BWXT Idaho, LLC (BBWI) Internal Report, *Operable Unit 1-07B Fiscal Year 2001 Well Maintenance Report* (INEEL 2002).
August 13,2001	Complete loss of power at TAN, probably due to weather.
November 15,2001	A port-a-reel pump was deployed in TAN-37 to 275 ft below land surface (bls) to sample at the B depth.
December 3-4.2001	Pump on the port-a-reel deployed in TAN-37 would not work. Variable frequency drive (VFD) pump controller failed on ground fault.
December 4,2001	The generator ran out of gas after TAN-25 was purged, but before samples were collected. The generator was filled with gas, TAN-25 was purged for 5 minutes, and then samples were collected.
December 6,2001	A portable pump was placed in TAN-37 at 272 ft bls to sample at the B depth.
December 10,2001	TAN-37 was sampled the week following collection of samples from the rest of the ISB wells due to problems with pumps placed in TAN-37.
January 7,2002	Began using newly constructed sample boards during ISB sampling. The pump at TAN-37C would not work, so a port-a-reel was deployed.
January 8,2002	Problems with VFD, getting ground fault error.
January 8,2002	The liner in the influent tubing on the new sample board had failed due to the cold weather, so it was replaced with new clear plastic tubing.
February 4,2002	Problems with the new sample boards. The lower portions of the flow meters broke on both new sample boards, possibly due to the temperature difference between the groundwater and the cold winter air. Stainless steel replacements were ordered. Longer inlet hoses were made with Tygon tubing that is not Teflon lined.
February 4,2002	A document action request (DAR) was completed to use the old sample boards for sampling.
February 5, 2001	The Radiological Work Permit (RWP) was revised to Wear A requirements for dress and thermoluminescent dosimeters (TLDs) are required for entering any controlled area or when handling samples.
February 13,2002	When removing Hydrolabs from TAN-37, a noise was noted from the well sounding like gas percolating through the well at a slow rate.

Date	Issue
February 18,2002	**A** Radiological Control Technician (RCT) **and** an Industrial Hygienist (IH) conducted radiological surveys and performed organic vapor, H_2S, and lower explosive limit monitoring at TAN-37 to **try** to determine the source of bubbling noise observed on February **13,2002,** but the noise was not observed during this monitoring.
February 26,2002	Flow meters on the new sample boards were repaired and stainless steel bushings installed.
March 5,2002	Two attempts were made to use the pump in **TSF-05,** but it would not bring water to the surface. The pump was pulled to the surface **and an** RCT determined it was too radiologically hot to remove. Later that same day, RadCon approved removal of the pump from the well. Radiation on the hose was natural.
March 13,2002	Installed a replacement pump in **TSF-05.**
April **17,** 2002	IH was present to perform exposure monitoring during sample collection at TAN-37.
April 29, 2002	Flow through cells on new sample boards were changed.
April 30,2602	IH was present to perform exposure monitoring during sample collection and created a window opening between laboratory sea vans located inside **the** Groundwater Treatment Facility (GWTF) tent for additional air circulation.
May 8,2002	TAN-25 microbiological samples were collected again because excessive aeration was present for samples collected from **TAN-25** on May 6,2002.
June 26,2002	Bangboard is operational.
July **8,2002**	The VDF box tripped the bangboard breaker, so the bangboard could not be used for sampling. The generator was **used** instead.
August 19,2002	Sample board Hydrolab flow-through **cell** and gal/minute gauge changed because the plastic pieces had cracks.
August 20,2002	The reels for the pumps in **TAN-37** were reported to be deteriorating so bad that they may not be usable for the next **ISB** sampling round.

III. TSF-05 Pump Placements and Sampling

The date and time pumps were placed and samples were collected from TSF-05A and TSF-OSB are **listed in** Table **A-4.**

Table **A-4.** Pump placements for TSF-OSA **and** TSF-OSB.

TSF-OSA		TSF-05B	
Date/time pump placed at TSF-OSA.	**Date/time sample collected at TSF-OSA.**	**Date/time pump placed at TSF-OSB.**	**Date/time sample collected at TSF-05B.**
Placed at A (235 ft) on August 7,2001 **at** 1312	**August** 7,2001 at **1340**	Placed at B (269 ft) on August 7,2001 around 1100	August 7,2002 at 1245

Table **A-4.** (Continued).

TSF-05A		TSF-05B	
Date/time pump placed at TSF-OSA.	**Date/time sample coliected at TSF-05A.**	**Date/time pump placed at TSF-OSB.**	**Date/time sample collected at TSF-OSB.**
Placed at **A on** September 10,2001 first thing in the morning	September 11,2001 at 1045	Placed at **B** (270 ft) on September 11,2002 at 1105	September 12,2001 at 0825
Placed at **A** on October 4,2001	October 8,2002 at 1426	Placed at B (269 ft) on October 8,2001 **after** sample collection ***at*** **A**	October 10.2001 **at** 1114
No record	November 6,2001 at 1025	No record	November 7,2001 at 0900
Placed at **A** (235 ft) on November 29,2001	**December** 3,2001 at 1020	No record	December 4,2001 at 1000
No record	**January** 7,2002 at **1408**	Placed at B on **January** 7,2002 at **1454**	January 8,2002 at 1456
No record	**February** 4,2002 at 1513	No record	**February** 5,2002 at 0954
Placed at **A** (220ft) on February 5,2002 **at** 1010	March 4,2002 at 1407	No record	**Not** sampled due to **inoperable** pump.
No record	**April** 1,2002 **at 1328**	No record	April 2,2002 ***at*** 1049
Placed at **A** on **April** 25,2002	**April** 30,2002 at 1104	No record	May 1,2002 at 1330
No record	June 3,2002 at 1345	No record	**June** 4,2002 at 0835
Placed at **A** on **July** *3,* 2002	July 8,2002 at 1244	No record	July 9,2002 1042
No record	**August** 5,2002 at 0908	No record	**August** 6,2002 at 0857
No record	September 9,2002 at 1007	Placed at B immediately following sample collection at **A.** All ISB samples collected **in** 1 **day** to allow for GWTF **flushing.**	September 9,2002 at 1519.
No record	October 7,2002 at 1249	No record	October 8,2002 at 1105

IV. Curtailment of Daily Inspections

Actions **taken** to remove hazardous **waste from** the Air Stripper Treatment **Unit (ASTU) and** GWTF **are detailed** in following two **letters:**

INEEL
BECHTEL BWXT IDAHO, LLC

P.O. Box 1625
2525 North Fremont Ave.
Idaho Falls, Idaho 83415
(208) 526-0111

July 6, 2001

CCN 23376

Kathleen E. Hain
Environmental Restoration Program
U.S. Department of Energy
Idaho Operations Office
850 Energy Drive, MS 1117
Idaho Falls, ID 83401-1563

CONTRACT NO. DE-AC07-99ID13727 – CURTAILMENT OF DAILY INSPECTIONS OF THE AIR STRIPPER TREATMENT UNIT AND THE GROUNDWATER TREATMENT FACILITY

Reference: Kathleen E. Hain letter to Dean Kygard and Wayne Pierre, EM-ER-01-109, Curtailment of Daily Inspections of the New Pump and Treat Facility, June 19, 2001

Dear Ms. Hain:

The referenced letter describes curtailment of daily inspections of the New Pump and Treat Facility (NPTF) when the system does not contain hazardous waste. Similarly, curtailment of the daily inspection requirement for the Air Stripper Treatment Unit (ASTU) and the Groundwater Treatment Facility (GWTF) has been discussed with the FFA/CO Agencies in conference calls held on June 7, 2001, and June 14, 2001. During these discussions, the Agencies agreed that daily inspections are not required for these systems when they do not contain hazardous waste. Based on these discussions and understanding, the following actions are proposed to remove the hazardous waste from each of the two systems.

Removal of hazardous waste from the ASTU would be performed per the following steps:

- Flush the ASTU by processing potable water through the system. During processing, the air stripper and blower will be operating and the effluent water will be injected into well TAN-49 (ASTU injection well).
- Sample residual water remaining in the air stripper sump and analyze for trichloroethene (TCE) using the Solid Phase Micro Extraction (SPME) method. If the TCE concentration is less than 5 µg/L then it will be determined that the hazardous waste has been removed.
- Repeat flushes as needed until the concentration of TCE in the ASTU sump is less than 5 µg/L.

Removal of hazardous waste from the GWTF would be performed as follows:

- Empty the resin columns. (Ion exchange resin will be packaged and stored in the CERCLA waste storage units).
- Recirculate potable water through tanks T-2 and T-3 until all residual solids are removed. Process and inject this water into the GWTF injection well, TAN-31.
- Remove all bag filters.
- Remove sand and gravel from the multimedia filter. (Sand and gravel will be packaged and stored in the CERCLA waste storage units).
- Flush all tanks and piping with potable water.
- Sample the effluent from tank T-2 (SP-4) for TCE and analyze for TCE concentrations using the SPME method. If the TCE concentration is less than 5 µg/L then it will be determined that the hazardous waste has been removed from the tanks and piping system.

- Repeat system flushes as needed until the concentration of TCE in the GWTF effluent is less than 5 µg/L.
- Empty the carbon beds. (Carbon will be packaged and stored in the CERCLA waste storage units).

Once hazardous waste has been removed from each of these systems, daily inspections are no longer required and will not be performed until they again hold hazardous waste. Please advise us by July 16, 2001, if the above does not accurately reflect our agreement; otherwise, BBWI will implement this action.

Please contact Lee Nelson at 526-3093 if you have questions regarding this transmittal.

Sincerely,

F. Lee Smith, Manager of Projects
Environmental Restoration

LON:mr

Attachment

cc: R. J. Hoyles, DOE-ID, MS 1221
L. A. Sehlke, MS 3810
R. Mark Shaw, DOE-ID, MS 1117

K. Nelson
3921

Department of Energy
Idaho Operations Office
850 Energy Drive
Idaho Falls, Idaho 83401-1563

October 15, 2002

Mr. Wayne Pierre, Team Leader
Environmental Cleanup Office
U.S. Environmental Protection Agency
Region X
1200 Sixth Avenue
Seattle, Washington 98101

Mr. Dean Nygard, Site Remediation Manager
Idaho Department of Environmental Quality
1410 N. Hilton
Boise, Idaho 83706

SUBJECT: Curtailment of Groundwater Treatment Facility Daily Inspections (EM-ER-02-173)

Reference: Kathleen E. Hain letter to Dean Nygard and Wayne Pierre, Curtailment of Daily Inspections of the Test Area North Air Stripper Treatment Unit and the Groundwater Treatment Facility, July 2001

Dear Mr. Pierre and Mr. Nygard:

The referenced letter lists the actions required to allow curtailment of daily inspections of the Groundwater Treatment Facility (GWTF). The required actions are;

- Empty the resin columns.
- Recirculate potable water through tanks T-2 and T-3 until all residual solids are removed. Process and inject this water into the GWTF injection well, TAN-31.
- Remove all bag filters.
- Remove sand and gravel from the multimedia filter.
- Flush all tanks and piping with potable water.
- Sample the effluent from tank T-2 (SP-4) for trichloroethene (TCE) and analyze for TCE concentrations using the Solid Phase Micro Extraction (SPME) method. If the TCE concentration is less than 5 µg/L then it will be determined that the hazardous waste has been removed from the tanks and piping system.
- Repeat system flushes as needed until the concentration of TCE in the GWTF effluent is less than 5 µg/L.
- Empty the carbon beds.

The actions listed above have been completed. As agreed to in the referenced letter, the GWTF effluent was analyzed using the SPME method. The concentration of TCE found in the GWTF effluent was less than the detection limit of 0.9 µg/L. The concentration of TCE found in the rinse water was less than

the specified level of 5 µg/L. For your information, a comparison between historical OU 1-07B analytical results obtained using the SPME method and the EPA 8260B method is attached. Based on the attached historical information and Agency agreements detailed above, daily inspections of the GWTF may be curtailed.

After the above steps were completed, residual water was drained from the GWTF process equipment and piping. As of October 2, 2002, all GWTF process equipment has been deemed non-operational and is being stored within the existing secondary containment until the final disposition is determined. Starting October 25, 2002, GWTF inspections will be done weekly as is currently performed for other OU 1-07B CERCLA waste storage areas. The procedures and checklists used to conduct the OU 1-07B waste storage area inspections will also be used to inspect the GWTF.

If you have any questions regarding this issue please contact Mark Shaw at (208) 526-6442.

Sincerely,

PMShaw for

Kathleen E. Hain, Manager
Environmental Restoration Program

Attachment

cc: M. Jeffers, DEQ, 1410 N. Hilton, Boise, ID 83706

Comparison Between SPME and EPA 8260B Analytical Results for Chloroethenes.

The Operable Unit (OU) 1-07B program routinely uses the Solid Phase Microextraction Method/gas chromatography-electron capture detector (SPME) method for measuring chloroethene concentrations in groundwater. Split samples are routinely submitted for both SPME and EPA 8260B analysis and compared. The trichloroethene (TCE) concentrations for the past two years of split samples are presented in Table 1 for New Pump and Treat Facility integrated test data and Table 2 for in situ bioremediation (ISB) performance monitoring data. (Refer to the ISB Annual Report for October 1999 to July 2001, INEEL/EXT-2002-00543, Revision 0, for more complete description of the ISB results.)

Table 1. Trichloroethene sample results for SPME vs. EPA 8260B analyses for New Pump and Treat Facility integrated testing.

Sample Date	Sample Location (Air Stripper #)	TCE		Relative Percent Difference (RPD)
		SPME	8260B	
5/1/2001	A311	ND	ND	–
5/1/2001	A310	ND	ND	–
5/8/2001	A310	5.5	4.5	18
5/8/2001	A311	5.6	5.3	5
5/10/2001	A310	5.8	5.5	5
5/16/2001	A310	5.8	5.5	5
5/16/2001	A310	5.3	5.5	4
5/16/2001	A311	3.6	3.9	8
5/16/2001	A311	3.7	3.9	5
7/10/2001	A310	4.6	4.4	4
7/10/2001	A311	3.2	2.9	9
7/10/2001	A311	3.2	2.9	9
7/11/2001	A310	2.9	3.0	3
7/11/2001	A311	3.0	3.0	0
8/7/2001	A310	2.5	4.7	88
8/7/2001	A311	2.5	3.1	24
8/8/2001	A310	4.1	4.9	20
8/8/2001	A311	2.6	3.2	23
			Mean RPD	14 ± 21.1

ND = Not detected

Table 2. Mean RPD for SPME vs. EPA 8260B analyses for trichloroethene (TCE) from October 1999 to July 2001.

Chloroethene	Mean RPD for SPME vs. EPA 8260B results
TCE	20.24

The TCE concentrations shown in Table 1 varied from non-detect to 5.5 parts per billion (ppb). This range corresponds to TCE concentrations encountered during rinse out of the Groundwater Treatment Facility (GWTF). The mean relative percent difference between the SPME and the EPA 8260B data is 14%. The data in Table 2 indicate that the RPD for TCE analyses completed in support of ISB performance monitoring was less than 25%. Review of the split data from both NPTF integrated testing and ISB performance monitoring did not reveal any instances where the concentration of TCE exceeded the MCL and was not detected by the SPME method. As a result, these data show that the results obtained by the SPME method are acceptable for the purposes of curtailing GWTF inspection.

V. Waste Management

Issues directly affecting waste management activities are detailed in Table A-5.

Table **A-5.** Issues affecting waste management **activities.**

Date	Issue
October 11, 2001	**Water** used at the IRC in the bioreactor was added **as** a source **of** F001 waste in the waste determination.
October 31, 2001	Discussions took place to determine whether to use soap and water **or** bleach and water to rinse the sample boards **and** accessories. It was decided to use bleach and water because this could be added **as** a source of F001 waste in the waste determination.
November *29,* 2001	Set **up** system to rinse sample boards and accessories **with** bleach and water.
January *8,2002*	Began rinsing sample boards and accessories with bleach and water.
January *23,2002*	IRC bioreactor **waste** was placed in the New Pump and Treat Facility (NPTF) to be injected at 500:1 ratio.
April *25, 2002*	**A** D002 waste carboy was mistakenly dumped in the 500:1 purge water container. The contents of the 500:1 container **were** transferred into a **poly** drum for proper storage.
June *24,2002*	Authorization was given to **discharge** potable water into a manhole east of the GWTF. Potable water was used in preparation for the tracer test.
July 11,2002	Determined the amount and concentration of nickel nitrate solution to **be** used during the **ISB** tracer test. Waste Generator Services **(WGS) set up an** appropriate waste stream for **the** nickel nitrate solution.
August 2,2002	TAN-26 purge water was mistakenly put in **a** 5001 processing ratio **tank.**

VI. References

INEEL, January 2002, BBWI Internal **Report,** ***Operable Unit I-07B*** *Fiscal Year 2001* ***Well Maintenance Report,*** INEEL/INT-01-01431, Revision 0, **Idaho** National Engineering and Environmental Laboratory, Idaho Falls, Idaho.